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Metal-semimetal Schottky diode relying on quantum confinement

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Abstract

Quantum confinement in a semimetal thin film such as bismuth (Bi) can lead to a semimetal-to-semiconductor transition which allows for the use of semimetals as semiconductors when patterned at nanoscale lengths. Bi native oxide on Bi thin film grown by molecular beam epitaxy (MBE) is investigated using X-ray photoelectron spectroscopy (XPS) to measure the elemental composition of the oxide. Also, an *in-situ* argon plasma etch step is developed allowing for the direct coating of the surface of thin Bi films by a metal contact to form a Schottky junction. Model structures of rhombohedral [111] and [110] bismuth thin films are found from density functional theory (DFT) calculations. The electronic structure of the model thin films is investigated using a *GW* correction and the formation of an energy band gap due to quantum confinement is found. Electrical characterization of the fabricated Bi-metal Schottky diode confirms a band gap opening in Bi thin film for a film thickness of approximately 5 nm consistent with the theoretical calculations.

Highlights

Growth and characterization of high quality crystalline Bi
Study of elemental composition of the Bi native oxide using XPS
Employing quantum confinement induced band gap in Bi film to make Schottky diode

Keywords: Bismuth; Native Oxide; Quantum Confinement; Schottky Junction; Semimetal; XPS

1. Introduction

Nanoscale field-effect-transistors (FETs) enable the continuation of Moore's law for future technology generations, permit high device density at lower power per device, and consequently high function per integrated circuit at lower unit cost. However, for channels in the sub-7nm regime, the discrete nature of dopant atoms poses challenges for the formation of junctions on the nanoscale. Achieving typical impurity concentrations for nanoscale devices means relying on the addition of very few dopant atoms [1].Coupled with non-uniformities in the impurity concentration [2,3] leads to severe variability in the performances of transistors with geometries at critical dimensions below 7 nm [4,5]. For critical dimensions of a few nanometers, quantum confinement has a pronounced effects on electronic band structures. Bulk bismuth displays unique electrical properties such as extremely high electron mobility. The atomic bonding in Bi creates diverse structures and surfaces, such that it can be viewed as intermediate to 2D and 3D materials. Low dimensional Bi has been investigated for thermoelectric properties [6]. Quantum confinement in a low-dimensional semimetal such as bismuth leads to a semimetal-to-semiconductor transition as the physical size of a nanostructure becomes comparable to the Fermi wavelengths of electrons and/or holes [7]. This property can be used to enable the formation of a semiconducting channel between semi-metallic source and drain regions in a confinement modulated gap transistor (CMGT) architecture [8] eliminating the requirement for introducing dopant atoms into nanostructures. Formation of a hetero-dimensional rectifier in a single bismuth nanolayer consisting of a thicker three dimensional (3D) semimetallic region abutting a thinner two dimensional (2D) region that is semiconducting junction due to quantum confinement has recently been reported [9]. In that work, a procedure for removing the native oxide using an Ar plasma etch to strip the interfacial oxide layer allowing for the formation of a metal/Bi interface. This junction forms a Schottky barrier if the quantum confinement effect is large enough to open a band gap in the thinner semimetallic film. Achieving a band gap several times larger than the thermal energy (k_BT) at room temperature needed for practical nanoelectronics applications, requires confinement dimensions of <10nm in Bi [10]. The band gap increase due to quantum confinement in semimetals at a few nanometer

length scales can be engineered to be comparable to conventional semiconductors sued for electronics applications [8,10,11].

2. Bi film growth and characterisation

Bi films used in this study were grown by molecular beam epitaxy (MBE) on undoped Si [111] wafers. Prior to the deposition, the Si substrates were chemically cleaned by the HF-last RCA procedure to remove the native oxide and to passivate the surface with hydrogen. The substrates were subsequently heated *in-situ* to 700 °C for 20 minutes to desorb the hydrogen atoms from the Si surface. The Bi material flux was generated by an effusion cell operated at a temperature of 550 °C, which yields a growth rate of 17 nm/hour. Thickness and crystallographic orientation are the key parameters determining the resulting electronic structure of the thin films. A high-resolution cross-sectional transmission electron microscopy (HR-XTEM) image of the 4.5 to 5 nm film is shown in Fig. 1 and is consistent with the high quality single crystal nature of bismuth thin films. Presence of Bi native oxide on the Bi thin film grown by MBE is also seen within the TEM image. Hall measurement of the Bi thin films indicates high mobility for this ultra-thin film which suggests that the native oxide does not result in a considerable surface scattering [9].

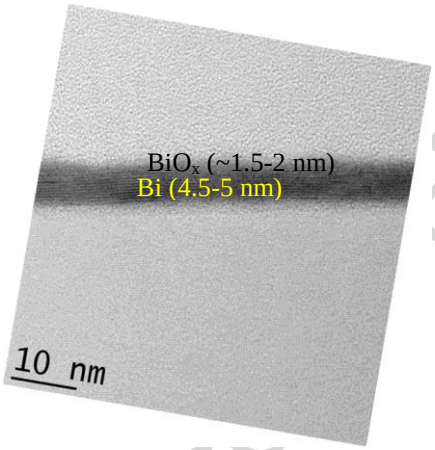


Figure 1: HR-TEM image of the MBE-grown Bi thin film showing the native Bi oxide.

To investigate the native bismuth oxide, X-ray photoelectron spectroscopy (XPS) was performed to verify the elemental composition of the surface. XPS data from sputtering studies was collected using a Kratos AXIS-ULTRA instrument with a monochromatic Al-K_α X-ray source at 150 W power and the spectra were obtained using a pass energy of 160 eV for survey spectra, and with 20 eV for narrow core level regions with a surface take-off angle of 45°. Depth profiling was carried out using a gas cluster ion source of Ar_{500+} (5 keV, 3 mm^2 raster size) and the spectra were acquired at different sputter times as indicated in the Fig.2.

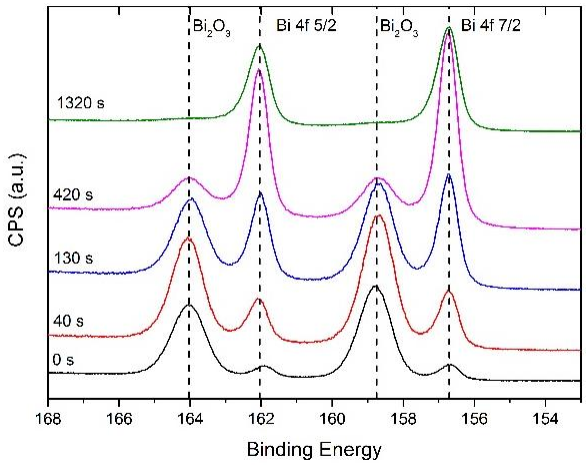


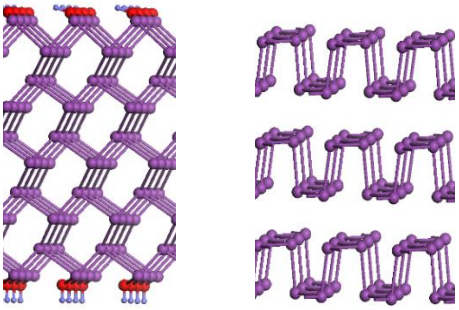
Figure 2: X-ray photoelectron spectroscopy (XPS) of Bi film after various intervals of Ar etch.

The cluster allowed for gentle sputtering of the film without damaging the underlying Bi substrate. As shown in Fig. 2, it was possible to completely remove the oxide from the surface and obtain an XPS spectrum for the bare Bi sample. Fig. 2 displays the Bi *4f* core level spectrum collected after subsequent sputtering times. As the sputtering time increases, the Bi *4f* components at 156.7 eV (Bi *4f* 7/2) [12] and at 162.0 eV (Bi *4f* 5/2) [13] increase in intensity until, after 1320 s, the Bi_2O_3 peaks at 158.6 eV [14] and at 163.9 eV [15] disappear and only elemental Bi remains present on the surface.

3. Theory and simulations

Bi is a pentavalent post transition metal in group V and has a rhombohedral crystal structure. Normal to the rhombohedral [111] orientation, *i.e.* along the C_3 symmetry axis, the structure can be considered as a stacked bilayers with three nearest neighbor bonds for each atom within a single bilayer. Each bilayer has a puckered structure with each 'up' atom forming three weaker bonds to atoms in the next upper bilayer and the three 'down' atoms in the bilayer forming three weaker bonds to the next lower bilayer. The stronger intralayer bonding and weaker interlayer bonding results in a 2D stacked structure.

The weak bonding between bilayers leads to a strong sensitivity for the electronic structure in a thin bismuth film due to the surface terminating chemistry. It is known that upon exposure to air that a surface oxide forms. Within density functional theory (DFT) calculations, introduction of a single hydroxyl (-OH) group to a (111) surface bilayer results in significant reconstruction as resulting surface bonding is stronger than bonds between Bi bilayers. In contrast, for a (110) Bi surface, an even number for each layer provides stable configuration [16].



(a) (b)

Figure 3: Atomic illustration of Bi thin film along (a) [111] and (b) [110] crystallographic orientation after geometry optimization.

DFT is standard method to study the atomic and electronic structure of materials. However, DFT methods are well known to suffer deficiencies with respect to predicting band gaps primarily due to commonly used approximations for the electronic exchange and correlation energies. These approximations typically result in a large and systematic underestimation of band gaps in semiconductors. The semimetallic behavior of bulk Bi using DFT predicts a much larger band overlap of ~160 meV [17,18] when compared to the experimental value of approximately 40 meV [19]. To provide an improved description of the confinement effect in bismuth thin films, particularly with respect to determining band gap energies, the *GW* (*G*: Green's function, *W*: screened Coulomb interaction) method in conjunction with a first order many body perturbation theory (MBPT) correction is used [20] based on the Kohn-Sham DFT solutions [21]. The local-density approximation (LDA) for the exchange-correlation potential and norm-conserving pseudopotentials are used with an energy cutoff of 60 Rydberg for the plane-waves used as in the expansion of the Kohn-Sham solutions. Optimisation of the Bi film structures used in for the *GW* calculations is achieved by minimisation of the total DFT energy with respect to the atomic positions until the maximum force component becomes less than 0.01 eV/Å. Periodic boundary conditions are applied creating simulation supercells and the cell dimensions transverse to the slab surfaces are chosen to be greater than 2 nm to suppress the interaction between periodic images. The DFT and *GW* calculations are performed with non-relativistic pseudo-potentials and without the inclusion of spin-orbit interactions which are known to be considerable in bismuth [22]. The effect of spin orbit coupling and more detailed studies of the influence of surface termination on the (111) surface will be included in future investigation of the Bi electronic structure calculations. The surface chemistry in bismuth thin films and nanowires (NWs) plays a crucial role on electronic structure due to weak orientation dependence of the semimetallic bonding and due the weak interlayer bonding. To correlate the electronic structure calculations with the experimental results reported in this work, explicit metal/bismuth interface models are required. The weak bonding between bismuth bilayers and a weaker orientational dependence in general for semimetallic bonding relative to conventional semiconductors introduce subtleties to the surface models that are the subject of ongoing exploration.

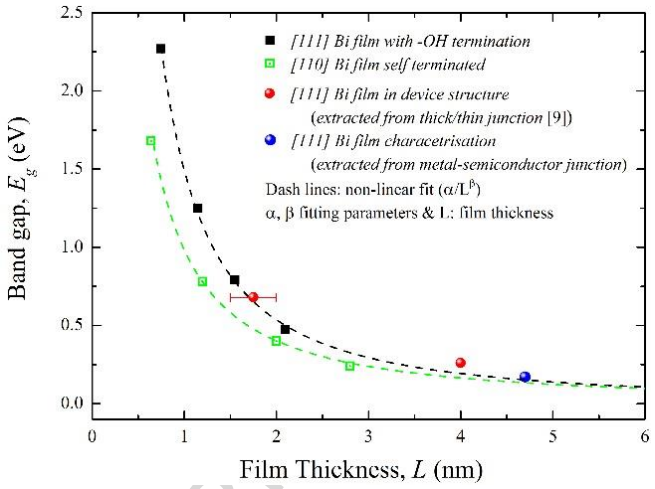


Figure 4: Band gap versus film thickness from GW calculations for Bi (111) and (110) slabs. The dashed curves show a power law fit α/Lβ where L is the film thickness and α, β are fitting parameters. The blue sphere is extracted from thin film electrical characterization data. Red spheres are experimental estimates based on extraction from the current-voltage (IV) characteristics at different temperatures for thick/thin bismuth junctions [9].

Our initial results on the thin bismuth layers is presented in Fig. 4 which indicates the magnitude of the quantum confinement effect as a function of film thickness. The calculations suggest that for a few bilayers, relatively large band gaps are achievable – however, the effects of spin orbit and surface chemistry need to be further explored to make quantitative estimates of the band gap.

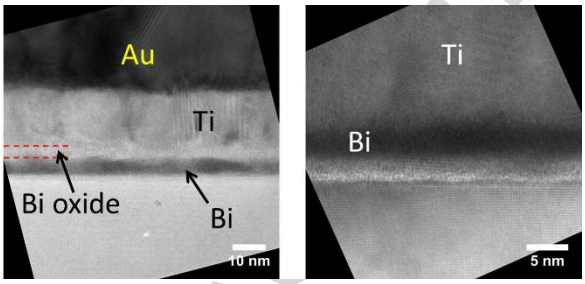
4. Metal-semiconductor Schottky junction

To form a metal-semimetal junction, the Bi native oxide needs first be removed. To do so, and to prevent exposure of the Bi films to oxygen following oxide etch, an Ar plasma etch step was developed to allow coating the etched surface *in-situ* with a titanium contact without the need to break vacuum. Fig. 5(a) shows HR-TEM images of the metal/Bi film interface with and without the Ar plasma surface treatment. Clear to see in Fig. 5(a) is that the plasma surface treatment successfully removes the native Bi oxide without destroying the Bi thin film. Circular transfer length method (cTLM) structures are patterned using the Ar surface treatment. Electrical characteristics of the cTLM structure at temperatures of -40 °C and 40 °C are presented in Fig. 5(c), indicating Ohmic behavior at the higher temperature and Schottky behaviour at lower temperature. This is the experimental evidence of semiconducting characteristic of ultra-thin Bi films due to quantum confinement at temperatures close to room temperature as opposed to cryogenic temperatures [23].

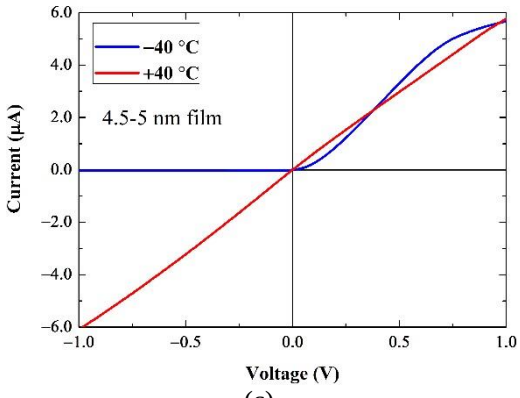
The electrical characteristic of the Bi Schottky diodes made using Ar plasma surface treatment are shown in Fig. 5(d) over narrower voltage and current ranges than in Fig 5(c). The activation energy derived from the temperature dependent IV characteristics is 80-90 meV (i.e., band gap of 160-180 meV assuming a mid-gap alignment of the Fermi level in the quantum confinement induced band gap in the Bi film) which is of the same order of magnitude as the theoretical *GW*

prediction; see the experimental values marked with a blue sphere in Fig. 4. Due to thermionic emission over rather small band offset, i.e., 80-90 meV, at the metal/Bi junction, at room temperature carriers gain sufficient thermal energy to flow over the barrier; hence linear characteristic. While at low temperatures such as -40C thermionic emission is suppressed and therefore the rectification due to band offset is more pronounced. As expected due to thermionic emission over an energy barrier, the reverse current increases and the turn-on voltage decreases with increasing temperature. The diode current shows saturation effect at about 0.75 V at -40C as a result of reduction in carrier concentration [9] and hence increase in series resistance at lower temperatures. Electrical characteristic for the titanium-bismuth contacts made on thicker Bi film (28 nm) is shown in Fig. 5(e) fabricated with and without surface treatment. As can be seen, the metal/Bi junction shows Ohmic behavior with improvement in contact resistance after removing the Bi surface reflecting that the current is not required to tunnel across a native Bi oxide following the surface treatment by the Ar plasma.

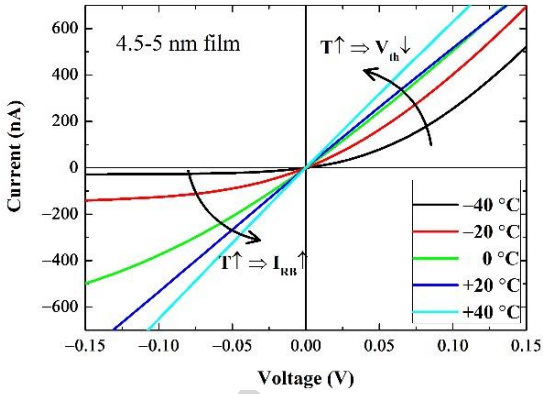
For nanostructured Bi to be useful in nanoelectronics applications, a band gap energy comparable to conventional bulk semiconductors is desirable. To achieve a larger confinement effect than what we report for Bi films, confinement in a second spatial dimension becomes necessary and hence leads to the use of NWs. Quantum confinement effects can be observed in NWs at larger critical dimensions as compared with thin films due to charge carriers being confined in two-dimensions [23]. However due to the larger surface-to-volume ratio for a nanowire, there are also stronger surface effects. For Bi, there is a strong electronic anisotropy and hence a nanowire's crystallographic orientation plays a strong role in electronic behavior.



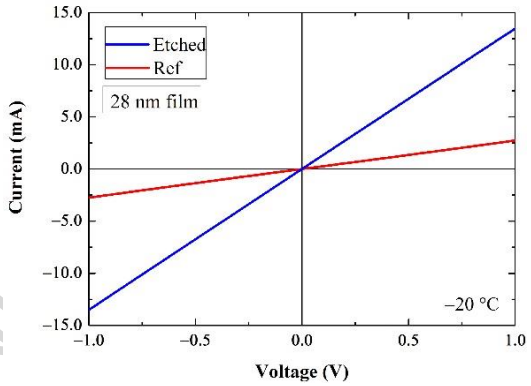
(a) (b)



(c)



(d)



(e)

Figure 5: HR-TEM images of metal/Bi interface (a) without, and (b) with oxide etch prior to metallization. Dashed lines in (a) show the Bi native oxide. IV characteristics of the ultra-thin film at low and high temperatures is shown in (c). Threshold voltage and reverse bias current variation with temperature is presented in (d). Impact of Bi oxide etch on the IV characteristics of the 28 nm Bi film at low temperature in (e) shows Ohmic behavior, confirming metallic feature.

Here we have laid the initial steps for processing of Bi (111) surfaces. Suppression of the XPS peaks associated with the bismuth native oxide by Ar sputtering demonstrates the ability to strip the native oxide while leaving a Bi layer that displays semiconducting behavior due to quantum confinement. Without breaking vacuum, titanium contact structures are patterned and electrical measurements at varying temperature reveal that a Schottky barrier is formed at the clean titanium-bismuth interface. The Schottky barrier height is consistent with preliminary estimates of the quantum confinement effect obtained by *GW* electronic structure calculations. Stronger confinement effects can be achieved by patterning bismuth NWs leading to band gaps relevant to room temperature nanoelectronics at larger critical dimensions than we consider. We further note that current commercial nanoelectronics technologies are achieving critical dimensions comparable to the Bi film thickness used to fabricate the metal-semimetal Schottky diodes presented in this work.

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References

[1] F. Iori, S. Ossicini, and R. Rurali, Conductance fluctuations in Si nanowires studied from first-principles, J. Applied Physics 116 (2014), 074303(1-4).
[2] M. V. Fernández-Serra, C. Adessi, and X. Blasé, conductance, surface traps, and passivation in doped silicon nanowires, Nano Lett. 6 (2006), 2674–2678.
[3] T. Markussen, R. Rurali, A. P. Jauho, and M. Brandbyge, Transport in silicon nanowires: role of radial dopant profile, J Comput Electron 7 (2008), 324–327.
[4] T. Markussen, R. Rurali, A. P Jauho, and M. Brandbyge, Scaling theory put into practice: first-principles modeling of transport in doped silicon nanowires, Phys. Rev. Lett. 99 (2007), 076803(1-4).
[5] R. Rurali, T. Markussen, J. Suñé, M. Brandbyge, A. P. Jauho, Modeling transport in ultrathin Si nanowires: charged versus neutral impurities, Nano Lett. 8 (2008), 2825–2828.
[6] X. Sun, Z. Zhang, and M. S. Dresselhaus, Theoretical modeling of thermoelectricity in Bi nanowires, Appl. Phys. Lett. 74 (1999), 4005-4007.
[7] Y. M. Lin, X. Sun, M. S. Dresselhaus, Theoretical investigation of thermoelectric transport properties of cylindrical Bi nanowires, Phys. Rev. B 62 (2000), 4610- 4623.
[8] L. Ansari, G. Fagas, J.-P Colinge, J. C. Greer, A Proposed Confinement Modulated Gap Nanowire Transistor Based on a Metal (Tin), Nano Lett. 12 (2012), 2222–2227.
[9] F. Gity, L. Ansari, M. Lanius, P. Schüffelgen, G. Mussler, D. Grützmacher, J. C. Greer, Reinventing solid state electronics: Harnessing quantum confinement in bismuth thin films, Appl. Phys. Lett. 110 (2017), 093111(1-4).
[10] L. Ansari, F. Gity, J. C Greer, Electronic and structural properties of rhombohedral [1 1 1] and [1 1 0] oriented ultra-thin bismuth nanowires, J. Phys. Condens. Matter 29 (2017), 065301(1-9).
[11] A. A. Nikolaeva, L.A. Konopko, T.E. Huber, P.P. BodiulI, A. Popov, E.F. Moloshnik, Size-quantization semimetal–semiconductor transition in Bi0.98Sb0.02 nanowires: thermoelectric properties, Journal of Elec. Materi. 41 (2012), 2313–2316.
[12] Kumar P.S.A., Mahamumi S., Nigavekar A.S., Kulkarni S.K., Reactivity and surface modification at a Bi/Bi2Sr2CaCu2O8 interface, Physica C 201 (1992), 145-150.
[13] F.M. Ismail, Z. M. Hanafi, Some Physico-Chemical Properties of Bismuth Chalcogenides x-Ray Photoelectron and Diffuse Reflectance Spectra, Phys. Chemie (Leipzig) 267 (1986), 667-672.
[14] K. Uchida, A. Ayame, Dynamic XPS measurements on bismuth molybdate surfaces, Surface Science 357 (1996), 170-175.
[15] B. Afsin, M. W. Roberts, Formation of an Oxy-Chloride Overlayer at a Bi (0001) Surface, Spectroscopy Letters 27 (1994), 139-146.
[16] T. Nagao, J. T. Sadowski, M. Saito, S. Yaginuma, Y. Fujikawa, T. Kogure, T. Ohno, Y. Hasegawa, S. Hasegawa, and T. Sakurai, Nanofilm Allotrope and Phase Transformation of Ultrathin Bi Film on Si (111)-7 × 7, Phys. Rev. Lett 93 (2004),105501(1-4).
[17] A. B. Shick, J. B. Ketterson, D. L. Novikov, and A. J. Freeman, Electronic structure, phase stability, and semimetal-semiconductor transitions in Bi, Phys. Rev. B 60 (1999), 15484 – 15487.
[18] I. Timrov, T. Kampfrath, J. Faure, N. Vast, C. R. Ast, C. Frischkorn, M. Wolf, P. Gava, and L. Perfetti, Thermalization of photoexcited carriers in bismuth investigated by time-resolved terahertz spectroscopy and ab initio calculations, Phys. Rev. B 85 (2012), 155139 (1-8).
[19] R. T. Isaacson, G. A. Williams, Alfvén-Wave Propagation in Solid-Stae Plasmas. III. Quantum Oscillations of the Fermi Surface of Bismuth, Phys. Rev. 185 (1969), 682-688.
[20] A. Marini, C. Hogan, M.Grüning, and D. Varsano, yambo: An ab initio tool for excited state calculations, Computer Physics Communications, 180 (2009), 1392–1403.
[21] Giannozzi P *et al*, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, J. Phys.: Condens. Matter 21 (2009), 395502 (1-19).
[22] Ph. Hofmann, The surfaces of bismuth: Structural and electronic properties, Progress in Surface Science 81 (2006), 191-245.
[23] S. Lee , J. Ham , K. Jeon, J. S. Noh, W. Lee, Direct observation of the semimetal-to-semiconductor transition of individual single-crystal bismuth nanowires grown by on-film formation of nanowires, Nanotechnology 21 (2010), 405701(1-6).
[24] J. P. Colinge, J. C. Greer, Nanowire Transistors: Physics of Devices and Materials in One Dimension, Cambridge University Press (2016).

Graphical abstract